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CERAMOGRANITE MADE FROM NATURAL MINERALS FOUND IN UZBEKISTAN

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A technology has been developed for manufacturing ceramogranite from natural materials found in Uzbekistan. The processes occurring during heat treatment of porcelain stone from the Boinaksaiskoe deposits have been investigated. The optimal calcination temperature, the composition of the ceramic paste, and the effect of individual components of the batch on the properties of ceramogranite have been determined. The kinetics of sintering of experimental pastes has been studied. It is shown that combining different types of mineral raw materials makes it possible to obtain ceramogranite with high thermomechanical characteristics.

Ceramogranite is a modern artificial material produced in the form of slabs. It can be classified as a sintered product with a porcelain-like structure, and it possesses novel properties distinguishing it from other ceramics. Owing to its high durability, low water absorption, and consequently high resistance to freezing, it can be used in any enclosures. Its special resistance to ultraviolet light makes it possible to use this material for paving roads and facing buildings. In addition, ceramogranite does not react to alkali or acids. In addition, unlike natural stone, ceramogranite does not emit background radiation. Special mineral additives add any color or color hue to ceramogranite.

The development of a technology for producing ceramogranite based on local raw materials is timely, since it creates real conditions for producing high-quality finishing material in Uzbekistan.

The possibility of obtaining ceramogranite was investigated on the basis of using porcelain stones from the Boinaksaiskoe deposit and kaolin from the Angrenskoe deposit. The processes which occurred during the treatment of porcelain stone from Boinaksaiskoe deposit have been investigated. The optimal calcination temperature, the composition of the ceramic paste, and the effect of individual components of the batch on the properties of the ceramic have been determined. The kinetics of calcination of experimental pastes has been studied.

The investigations were conducted using chemical, x-ray phase (DRON UM-1 diffractometer using copper radiation), and thermographic (Q 1500D Paulik system) methods of analysis were used.

Porcelain stones comprise a specific group of hydrothermally altered rocks, whose mineralogical and chemical properties are close to those of standard fine-ceramic pastes, which makes it possible to regard them as a form of complex ceramic raw material. They are distinguished by a fine-grain structure, low content of coloring oxides, and favorable mineral composition, which makes it possible to use them in ceramic pastes [1, 2].

X-ray phase analysis has shown that the main crystalline phase of porcelain rock of quartz-sericite type is quartz (55 – 60%[2]). Sericite type mica is present in smaller quantities (30 – 35%). Feldspar has not been detected by x-ray diffraction. This rock has virtually no manganese oxides, and it is characterized by low (on the average about 4.4%) quantities of alkali oxides with potassium greatly predominating over sodium (Table 1).

According to the chemical composition porcelain stones of the quartz-kaolinite-pirophyllite type should be classified as a non-alkaline high-quality raw material for the porcelain industry, and according to the mineral composition they should be classified as a pirophyllite quartz mineral type. This rock contains 10 – 15% quartz, 25 – 30% kaolinite, and 45 – 50% pirophyllite. An adequate content of quartz in the rock studied makes it possible to use it instead of the quartz component infine-ceramic pastes, and the presence of kaolinite and pirophyllite makes it possible to decrease the kaolin content in them.

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[2] Here and below — the mass content.

TABLE 1.

Raw material	Mass content, %								
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	calcination loss
Secondary Angrenskoe kaolin	59.33	26.70	0.32	1.52	0.27	0.40	1.10	0.22	10.10
Quartz-sericite rock	79.16	14.33	0.20	0.35	0.05	0.26	3.55	0.40	1.70
Quartz-kaolinite-pirophyltite rock	76.40	20.40	0.10	0.35	0.30	0.10	0.20	0.15	2.00
Wollastonite WK-2	53.30	2.27	0.10	1.30	38.60	1.40	0.53	0.10	2.40

The kinetics of calcination of porcelain stones and the character of the phase transformations were studied for samples of finely milled powders pressed under pressure 30 MPa. The samples were calcined in air in the temperature interval 560 – 1350°C. It was found that during heating of quartz-sericite porcelain stone at 560°C the sericite begins to decompose, which corresponds to an endothermal effect on the derivative curve. The process is completed at 1000°C. At higher temperatures the main crystalline phase is α-quartz, and mullite is also present. The amount of mullite with the calcination temperature up to 1400°C does not increase and equals 5% in this temperature interval. The data obtained established that the calcination of porcelain stone of quartz-sericite type starts at 1100°C. At 1250°C the apparent density reaches its maximum value (2.1 g/cm^3) with water absorption 0.04%.

During the calcination of quartz-kaolinite-pirophyllite rock at 560°C dehydroxylation and destruction of the crystalline structure of kaolinite occur, which results in vanishing of kaolinite in the diffraction pattern. At temperatures above 1100°C the peaks due to pirophyllite vanish, and the formation of mullite and a transition of α-quartz into cristobalite start. The amount of mullite grows slowly from 5 to 10% as the calcination temperature increases of up to 1350°C.

Thus, the final crystalline products of the phase changes of the rock are α-quartz, mullite, and cristobalite. On the derivative curve these phase transformations correspond to endothermal effects at 550 and 700°C and exothermal effects at 1000 and 1150°C. When the sample is heated, initially, these sample dimensions increase as a result of the behavior of pirophyllite, which expands during calcination, and as result of a transition of α-quartz into cristobalite. Calcination essentially does not occur at temperatures up to 1150°C, and water absorption is 19 – 20%. The calcination process is activated at temperatures above 1250°C, the shrinkage is 2.5 – 3.0%, and the water absorption of the samples decreases to 0.2%.

On this basis, compositions were developed for experimental fine-ceramic pastes based on Boinaksaiskoe porcelain stone, Angrenskoe secondary enriched kaolin, and Koitashskoe wollastinite concentrate. The chemical composition of the batch of experimental pastes is presented in Table 2. It should be noted that the technology for producing ceramogranite is close to the technology used to produce floor tiles. Specifically, preference is given to the wet method for preparing pastes. Fine grinding increases the reactivity with respect to the stone components of the pastes which are inert at normal temperatures, promoting break down of their structure.

The raw material components of the batch were carefully measured and ground together to a residue of no more than 1% on a No. 0063 sieve. The mixture obtained was dried to moisture content 5 – 7% and slabs were pressed under pressure 50 MPa, which were calcined at 1250 – 1300°C with the maximum temperature held for 1 h.

Reflections characteristic for quartz, mullite, cristobalite, and anorthite were observed in the diffraction pattern of samples of a paste with the optimal composition after calcination at 1250°C (see Fig. 1). It should be noted that the crystallization of mullite occurs immediately in the temperature range 1000 – 1100°C without the appearance of an intermediate spinel phase [3]. The formation of cristobalite in the experimental compositions occurs predominantly due to the quartz

TABLE 2.

Mass content wollastonite, wt.%	Mass content,* %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	calcination loss
5	72.94	18.32	0.63	2.11	0.29	1.75	0.27	3.52
10	71.78	17.41	0.68	4.02	0.35	1.76	0.25	3.54
12	71.32	17.05	0.70	4.79	0.37	1.77	0.27	3.55
14	70.85	16.69	0.70	5.55	0.41	1.77	0.26	3.56

* The TiO_2 content was 0.18% in all cases.

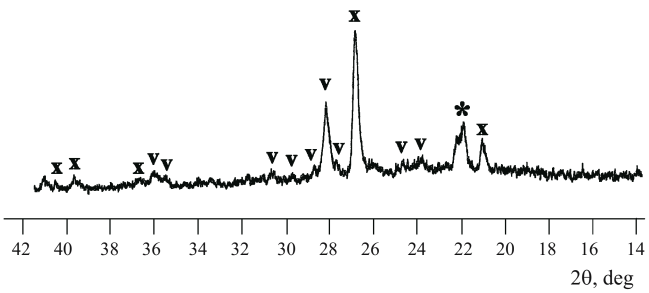

Fig. 1. Diffraction pattern of a sample of calcined ceramic (calcination temperature 1250°C, CuK_α radiation): **v**) anorthite, **x**) α-quartz, ★) cristobalite.

TABLE 3.

Properties of experimental pastes*	Wollastonite mass content, %			
	5	10	12	14
Calcination temperature, °C	1300	1300	1250	1250
Shrinkage, %	9.8	8.1	6.8	7.6
Water absorption, %	0.24	0.03	0.02	0.06
Ultimate bending strength, MPa	45	62	76	76

* In all cases, the heat resistance was 300°C and the durability was 0.08 g/cm^2.

from natural porcelain stone. The residual grains of quartz from quartz-pirophyllite raw material and also quartz formed when pirophyllite transforms into mullite can recrystallize into cristobalite, giving the ceramic material good mechanical properties. Some properties of calcined ceramic made from the experimental pastes are presented in Table 3.

The results of the investigations of the technological and physical-mechanical properties of the fine ceramic materials obtained showed that the maximum compaction of these samples made from the experimental pastes shifts, as the amount of wollastonite increases, to comparatively low temperatures. As one can see from the data in Table 3, increasing the content of wollastonite in the pastes intensifies the calcination process, since wollastonite is a strong flux and stimulates the process, lowering the temperature and decreasing the duration of calcination, and it also improves the thermomechanical properties because of the formation of anorthite — decrease of the fire shrinkage, increase of mechanical strength and heat resistance.

The complex of investigations and experimental works performed established that the natural minerals occurring in Uzbekistan can be used, in principle, as raw material for producing ceramogranite.

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